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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/DK96/00456 <b>(22) International Filing Date:</b> 4 November 1996 (04.11.96) <b>(30) Priority Data:</b> 1226/95 2 November 1995 (02.11.95) DK <b>(71) Applicant (for all designated States except US):</b> DANIONICS A/S [DK/DK]; Hestehaven 21 J, DK-5260 Odense S (DK). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> YDE-ANDERSEN, Steen [DK/DK]; Sønderdalen 32, DK-5260 Odense S (DK). RAO, Ningling [CN/DK]; Kesselstedet 3, Bramstrup, DK-5792 Årslev (DK). ANDERSEN, Torben, Paarup [DK/DK]; Rosenvænget 11, DK-5250 Odense SV (DK). <b>(74) Agent:</b> HOFMAN-BANG & BOUTARD, LEHMANN & REE A/S; Adelgade 15, DK-1304 Copenhagen K (DK).		<b>(81) Designated States:</b> AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> A NEGATIVE ELECTRODE COMPOSITION FOR LITHIUM SECONDARY BATTERIES, A METHOD FOR THE PRODUCTION THEREOF, USE OF SAID COMPOSITION IN LITHIUM SECONDARY BATTERIES AND LITHIUM SECONDARY BATTERIES CONTAINING SAID NEGATIVE ELECTRODE COMPOSITION		
<b>(57) Abstract</b>  The invention relates to a negative electrode composition for lithium secondary batteries comprising at least 10 % by weight of a carbon black having a specific BET surface area of at most 20 m <sup>2</sup> /g, preferably of 2 to 20 m <sup>2</sup> /g and a method for the production thereof wherein a carbon black and optionally a more ordered carbon material, preferably coke and/or graphite, is ground in a solvent containing a binder so as to produce a uniform, viscous slurry, followed by coating of the slurry onto a substrate, preferably a metal foil substrate, evaporation of the solvent and drying at elevated temperature. The invention also relates to the use of this negative electrode composition for the manufacturing of lithium secondary batteries as well as a lithium secondary battery comprising such a negative electrode composition.		

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A negative electrode composition for lithium secondary batteries, a method for the production thereof, use of said composition in lithium secondary batteries and lithium secondary batteries containing said negative electrode composition.

The present invention relates to a negative electrode composition for lithium secondary batteries, a method for the production thereof, use of said composition in lithium secondary batteries and lithium secondary batteries containing said negative electrode composition.

The immediate concept of the secondary lithium electrochemical cell was based on lithium metal negative electrodes, which, however, caused severe safety problems: Upon recharging of discharged cells, a non-uniform plating of lithium was observed on the electrode, which in terms led to the formation of dendrites, porous negative electrode structures, loss of active material, short-circuiting and thermal run-away (see e.g. Pistoia, G.: Industrial Chemistry Library, Vol. 5 (1994) pp. 1-47).

For these reasons the lithium metal electrode concept was substituted by the lithium-ion carbon-based electrode concept. According to the latter concept, lithium is intercalated into the carbon structure upon charging of the electrochemical cell (cf. Pistoia, G.: Industrial Chemistry Library, Vol. 5 (1994) pp. 1-47). Upon subsequent discharging of the cell, lithium is deintercalated from the carbon structure. This concept offers improved battery operation safety and cyclability as the main advantages. The capacity, however, is reduced compared to the pure lithium metal electrode. Furthermore, a substantial loss of capacity is observed due to the irreversible reactions between the carbon

material and the electrolyte (see e.g. Ebner, W. et al.: Solid State Ionics, Vol. 69 (1994) pp. 238-56).

5 The electrode capacity, the rate capability and cyclability are related to the physico-chemical characteristics of the constituent carbons (cf. Ebner, W. et al.: Solid State Ionics, Vol. 69 (1994) pp. 238-56). Ordered carbon structures like graphite are usually referred to as offering high reversible intercalation  
10 capacity, however poor cyclability and rate capability as the electronical conductivity is strongly reduced upon intercalation. Disordered carbon structures like carbon blacks are referred to as offering high electronical conductivity, however, to cause high irreversible  
15 capacity losses as the surface groups thereof react irreversibly with the electrolyte.

Mixtures of coke or graphite and carbon blacks provide electrodes with high electronical conductivity, even in  
20 the charged state. Therefore, addition of carbon black to a coke or graphite-based electrode improves the rate capability and cycle life compared to the pure coke- or graphite electrode (see e.g. Tarascon, J.M. and Guyomard, D.: Electrochimica Acta, Vol. 38-9 (1993) pp. 1221-31, EP  
25 434776 and JP 6-333559).

Heretofore, however, addition of carbon black to coke or graphite-based electrode structures has only been performed in order to raise the electronical conductivity  
30 of the electrode. It has in fact been reported that said addition is accompanied by an unwanted increase of the irreversible loss of capacity and a corresponding decrease in the electrochemical reversible capacity. Thus, whereas the capacity of pure coke electrodes is  
35 approximately 186 mAh/g, based on the  $\text{Li}_{0.5}\text{C}_6$

c mposition, the capacity of coke/carbon black mixtures is found to be lower.

In a paper of Dahn et al. in *Electrochimica Acta*, Vol. 38-39 (1993) pp. 1179-91 it is pointed out that high reversible capacities can be obtained for graphitic carbons as well as for carbons of high disorder. In addition, US-A-5 219 680 describes the use of microcrystalline or amorphous carbons as the essential component of lithium intercalation structures. The preferred amorphous carbons are of the acetylene black type, showing high surface area, in particular higher than 20 m<sup>2</sup>/g. In this case, however, the obtained irreversible capacity loss was high. More specifically, only 50-60% of the initial charge capacity was available as reversible capacity.

As the active lithium available in a rocking chair battery is provided by the lithium-containing positive electrode structure, the irreversible capacity loss is detrimental in terms of cell balance.

It is thus an object of the invention to provide a negative electrode composition for lithium secondary batteries offering improved performance in terms of capacity, rate capability, cyclability and reduced irreversible capacity loss compared to electrodes of the state-of-the-art.

According to the present invention this object is accomplished by a negative electrode composition comprising at least 10 % by weight of a low surface carbon black having a specific BET surface area lower than 20 m<sup>2</sup>/g, preferably of 2 to 20 m<sup>2</sup>/g.

The carbon black used according to the invention can be any low surface carbon black obtained through incomplete combustion or pyrolysis of hydrocarbons or natural gas, including low surface versions of channel black, furnace  
5 black, lampblack and thermal black. A detailed characterization of these carbon blacks and methods for the production thereof are given in "Recent Carbon Technology", JEC Press Inc., Edited by T. Ishikawa & T. Nagao (1983), and references therein.

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The preferred carbon black is selected from the group consisting of low surface area lampblacks prepared by incomplete combustion of aromatic hydrocarbons and low surface area thermal blacks prepared by pyrolytic  
15 decomposition of natural gas or methane.

WO 94/18714 of Valence Technology, Inc. describes the use of negative electrode structures comprising as well as particles of carbon, particles consisting of metals and  
20 semi-metals like aluminium, boron or silicon dispersed therein. The patent application, however, does not describe the advantages of using any carbon material of a BET surface area lower than  $20 \text{ m}^2/\text{g}$ , in contrast, describes as preferred embodiment, the use of high  
25 surface furnace blacks and acetylene blacks.

In an embodiment of the invention the negative electrode composition comprises a low surface area lampblack having a BET surface area of 5 to  $20 \text{ m}^2/\text{g}$ , preferably 15 to  $20 \text{ m}^2/\text{g}$ .  
30

It has been shown that cyclability as well as rate capability of the electrode composition according to the invention, depends on the absorption properties of the  
35 carbon black. This might be due to the fact that the DBP (dibutylphthalate) absorption relates to the degree of

structure of the carbon black. A high degree of structure provides high electronical conductivity and ease of dispersion.

- 5 The lampblack used according to this embodiment preferably has a DBP absorption of 50-200 ml/100 g, more preferably of 50-140 ml/100 g,

- 10 In another embodiment of the invention the negative electrode composition comprises a low surface area thermal black having a BET surface area of 2 to 20 m<sup>2</sup>/g, preferably 2 to 10 m<sup>2</sup>/g.

- 15 The thermal black used according to this embodiment preferably has a DBP (dibutylphthalate) absorption of 30-100 ml/100 g, more preferably of 30-80 ml/100 g.

- 20 The mean particle size of the carbon black used according to the invention is preferably within the range of 60 to 500 nm. It is even more preferred that the mean particle size is within the range of 60-150 nm in case of lampblacks and within the range of 100-500 nm for thermal blacks. Within these ranges the electronical conductivity, which is inversely related to the particle  
25 size, is still sufficient to ensure a high rate capability.

- 30 The most preferred lampblack is the Degussa Lampblack 101. The most preferred thermal black is the Kværner thermal black as produced by the Kværner CB&H process described in international patent application no. WO 93/20154.

- 35 The carbon black material used according to the invention may constitute the predominant part of the negative electrode or, alternatively, it may be present as an

additive in electrodes based predominantly on more ordered carbon structures such as coke or graphite.

Thus, in a preferred embodiment of the invention the negative electrode composition comprises at least 80% by weight, preferably at least 90% by weight, low surface area carbon black, the remaining part of the electrode composition essentially being a binder, preferably a polymeric binder.

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In another preferred embodiment of the invention the negative electrode composition comprises 10 to 90% by weight of a low surface area carbon black, 0 to 89% by weight of a more ordered carbon material, preferably coke and/or graphite, and 1 to 10% by weight of a binder, preferably a polymeric binder.

In yet another preferred embodiment of the invention the negative electrode composition comprises 10 to 40% by weight of a low surface area carbon black, 50 to 89% by weight of a more ordered carbon material, preferably coke and/or graphite, and 1 to 10% by weight of a binder, preferably a polymeric binder.

The "more ordered carbon material" used in this embodiment may be any carbon material having a higher degree of crystalline order than typical "carbon blacks", characterised in, that the interlayer spacing of "more ordered carbon materials" defined as half the length of the unit cell c-axis, is shorter than 3.44Å. More ordered carbon materials include cokes such as petroleum cokes produced by pyrolysis of petroleum residues, f.ex. by delayed coking or fluidized coking, gilsonite coke produced by coking of natural gilsonite, pitch coke produced by coking of coal tar pitch, f.ex. by the retort coking method or the delayed coking method, and



graphites such as natural or artificial graphite. A detailed characterization of these carbon materials and methods for the production thereof are given in "Recent Carbon Technology", JEC Press Inc., Edited by T. Ishikawa & T. Nagao (1983), and references therein.

The coke materials used in this embodiment preferably have a mean particle size of 1-50  $\mu\text{m}$  and a BET surface area of 8-20  $\text{m}^2/\text{g}$ . The most preferred coke materials are Lonza coke R-LIBA-A and Asbury #8442-R..

The graphite materials used in this embodiment preferably have a mean particle size of 1-50  $\mu\text{m}$  and a BET surface area of 5-40  $\text{m}^2/\text{g}$ . The most preferred graphite materials are Lonza Graphite KS6 and Asbury HPM 850.

The present invention is furthermore concerned with a simple and economically advantageous method for the production of a negative electrode composition for lithium secondary batteries, said electrode composition offering improved performance in terms of capacity, rate capability, cyclability and reduced irreversible capacity loss compared to electrodes of the state-of-the-art.

Thus, according to the invention a method is provided by which a carbon black and optionally a more ordered carbon material, preferably coke and/or graphite, is ground in a solvent containing a binder to produce a uniform, viscous slurry, followed by coating of the slurry onto a substrate, preferably a metal foil substrate, evaporation of the solvent and drying at elevated temperature.

The binder is preferably a polymeric binder, more preferably EPDM (ethylene-propylene-diene-polymethylene).

The solvent used in the electrode manufacturing process is preferably selected among alicyclic compounds, such as cyclohexane.

- 5 In the following examples I to V, production of various embodiments of the electrode composition according to the invention is illustrated.

#### Example I

10

2.6 g of coke (Lonza R-LIBA-A), 1.2 g of lampblack (Degussa lampblack 101) and 4.0 g of a 5% solution of EPDM (ethylene-propylene-diene-polymethylene; amorphous, oilfree, of medium saturation, ethylene content of 50%)  
15 in cyclohexane was introduced into a Ø100 mm porcelain mortar. The resulting mixture was subjected to 30 min. of grinding in order to mix the components and to produce a uniform slurry for coating. During mixing a further 7 g of cyclohexane was added. A portion of the slurry was  
20 poured onto a nickel foil substrate and spread out on the substrate by wirebar coating, thereby forming a uniform thin layer. The coated layer was kept in air for 20 min., and then dried in an oven at 110°C for 3 hours. The resulting negative electrode was tested in half cells  
25 against lithium metal, applying a lithium salt containing non-aqueous electrolyte. In the test the electrodes were charged and discharged galvanostatically between 0 V and 1.5 V vs.  $\text{Li/Li}^+$ . Irreversible capacity losses were derived from the first charge-discharge cycle, whereas  
30 the reversible capacity was defined as the first discharge capacity.

The obtained electrode having a composition of 65% by weight of coke, 30% by weight of lamp black and 5% by  
35 weight of binder, provided a reversible capacity of 240 mAh/g. The irreversible capacity loss was lower than 70

mAh/g, say lower than 22%. The discharge-charge cyclability of the produced electrode exceeded 300 cycles at 100% of the initial reversible capacity.

- 5 The reversible capacity of the said 240 mAh/g was obtained at a 1 hour discharge rate. Even at a 20 min. 3C discharge rate, the reversible capacity was 235 mAh/g.

10 Example II

1.9 g of lampblack (Degussa lampblack 101) and 2.0 g of a 5% solution of EPDM (ethylene-propylene-diene-polymethylene; amorphous, oilfree, of medium saturation, ethylene  
15 content of 50%) in cyclohexane was introduced into a Ø100 mm porcelain mortar. The resulting mixture was subjected to 30 min. of grinding in order to mix the components and to produce a uniform slurry for coating. During mixing a further 5 g of cyclohexane was added. A portion of the  
20 slurry was poured onto a nickel foil substrate and spread out on the substrate by wirebar coating, thereby forming a uniform thin layer. The coated layer was kept in air for 20 min., and then dried in an oven at 110°C for 3 hours. The resulting negative electrode was tested in  
25 half cells against lithium metal, applying a lithium containing non-aqueous electrolyte.

The obtained electrode having a composition of 92% by weight of lampblack and 8% of binder, provided a  
30 reversible capacity of up to 527 mAh/g. The irreversible capacity loss was lower than 264 mAh/g, say lower than 33%. The discharge-charge cyclability of the produced electrode exceeded 300 cycles at 100% of the initial reversible capacity.

The reversible capacity of the said 527 mAh/g was obtained at a 20 hour discharge rate. At a 24 min. (2/5 hour) discharge rate, the reversible capacity was 95 mAh/g.

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#### Example III

Using the manufacturing method and the test procedure described in Example II a negative electrode composed of  
10 95% by weight of thermal black (Kværner Carbon Black) and 5% by weight of binder (EPDM) was produced, said electrode providing a reversible capacity of 580 mAh/g, an irreversible capacity loss of 348 mAh/g, a discharge-charge cyclability of more than 20 cycles at 80% of the  
15 initial reversible capacity.

The reversible capacity of said 580 mAh/g was obtained at a 10 hour discharge rate. At a 12 min. (1/5 hour) discharge rate, the reversible capacity was 116 mAh/g.

20

#### Example IV

Using a lithium salt containing organic electrolyte, the manufacturing method and the test procedure described in  
25 Example I, a negative electrode composed of 63% by weight of graphite (Lonza Graphite KS6), 30% by weight of lampblack (Degussa Lampblack 101) and 7% by weight of binder (EPDM) was produced, said electrode providing a reversible capacity of 330 mAh/g, an irreversible  
30 capacity loss of 100 mAh/g, say 23% of initial capacity and a discharge-charge cyclability exceeding 300 cycles at 85% of the initial reversible capacity.

In the following example V production of lithium  
35 secondary batteries containing as negative electrodes an

electrod composition according to the invention is illustrated.

Example V

5 Electrochemical cells were prepared from laminates of negative electrode compositions of the above Examples I to IV, laminates of a transition metal oxide positive electrode coated on an aluminium foil, and sandwiched  
10 between said laminates an electrolyte composed of lithium salt in an organic electrolyte.

## Claims.

1. A negative electrode composition for lithium secondary batteries comprising at least 10% by weight of a carbon black having a specific BET surface area of at most 20 m<sup>2</sup>/g, preferably of 2 to 20 m<sup>2</sup>/g.
2. A negative electrode composition according to claim 1, in which said carbon black is a lampblack, a thermal black or any mixture thereof.
3. A negative electrode composition according to claim 2, in which said carbon black is a lampblack having a BET surface area of 5 to 20 m<sup>2</sup>/g, preferably 15 to 20 m<sup>2</sup>/g.
4. A negative electrode composition according to claim 3, in which said lampblack has a DBP (dibutylphthalate) absorption of 50-200 ml/100 g, preferably 50-140 ml/100 g.
5. A negative electrode composition according to claim 3 or 4, in which said lampblack has a mean particle size in the range of 60 to 150 nm.
6. A negative electrode composition according to claim 2, in which said carbon black is a thermal black having a BET surface area of 2 to 20 m<sup>2</sup>/g, preferably 2 to 10 m<sup>2</sup>/g.
7. A negative electrode composition according to claim 6, in which said thermal black has a DBP (dibutylphthalate) absorption of 30-100 ml/100 g, preferably 30-80 ml/100 g.
8. A negative electrode composition according to claim 6 or 7, in which said thermal black has a mean particle size in the range of 100 to 500 nm.

9. A negative electrode composition according to each of the preceding claims comprising at least 80% by weight, preferably 90% by weight, of said carbon black.

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10. A negative electrode composition according to any one of the claims 1 to 8 comprising 10 to 90% by weight of said carbon black, 0 to 89% by weight of a more ordered carbon material, preferably coke and/or graphite, and 1 to 10% by weight of a binder, preferably a polymeric binder.

11. A negative electrode composition according to claim 10 comprising 10 to 40% by weight of said carbon black, 50 to 89% by weight of a more ordered carbon material, preferably coke and/or graphite, and 1 to 10% by weight of a binder, preferably a polymeric binder.

12. A method for the production of a negative electrode composition according to any of the preceding claims, by which a carbon black and optionally a more ordered carbon material, preferably coke and/or graphite, is ground in a solvent containing a binder so as to produce a uniform, viscous slurry, followed by coating of the slurry onto a substrate, preferably a metal foil substrate, evaporation of the solvent and drying at elevated temperature.

13. A method according to claim 12, whereby the binder is a polymeric binder, preferably EPDM (ethylene-propylenediene-polymethylene).

14. A method according to claim 12 or 13, whereby the solvent is cyclohexane.

15. Use of a negative electrode composition according to any of the claims 1 to 11 for the manufacturing of lithium secondary batteries.

- 5 16. A lithium secondary battery comprising a cathode, a non-aqueous electrolyte including a lithium salt, and an anode, wherein the anode is constituted essentially of a negative electrode composition according to any of the claims 1 to 11.

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17. A lithium secondary battery according to claim 16, wherein the cathode is based on a transition metal oxide compound, preferably a vanadium oxide or a spinel lithium manganese oxide.

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 96/00456

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: H01M 4/36, H01M 10/40

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DIALOG: WPI, CLAIMS

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5219680 A (DENIS FAUTEUX), 15 June 1993 (15.06.93), column 2, line 24 - line 59; column 5, line 6 - line 34 --	1,12,15-17
A	Patent Abstracts of Japan, Vol 16, No 513, E-1283, abstract of JP,A,4-190561 (SANYO ELECTRIC CO LTD), 8 July 1992 (08.07.92) --	1
A	US 5028500 A (ROSAMARIA FONG ET AL), 2 July 1991 (02.07.91), column 4, line 2 - line 39; column 5, line 65 - column 6, line 20 --	1

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9418714 A1 (VALENCE TECHNOLOGY, INC.), 18 August 1994 (18.08.94), page 10, line 17 - page 11, line 4, abstract  -- -----	1-17

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

28/10/96

International application No.

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Patent document cited in search report		Publication date	Patent family member(s)		Publication date
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			CN-A-	1073302	16/06/93
			EP-A-	0528557	24/02/93
			JP-A-	5198298	06/08/93
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			EP-A-	0434776	03/07/91
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			EP-A-	0682817	22/11/95
			JP-T-	8506689	16/07/96